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(54) **Water-insoluble naphthalic acid imide dyestuffs.**

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Description

The present invention relates to water-insoluble naphthalic acid imide dyestuffs having fluorescence. More particularly, it relates to water-insoluble reactive dyestuffs which are capable of dyeing not only polyester and triacetate fibers but also nitrogen-containing fibers including polyurethane fibers-and polyamide fibers such as nylon, silk and wool with a fluorescent clear greenish yellow or orange color.

Heretofore, for dyeing nylon or polyurethane fibers, it has been common to employ acid dyestuffs or metal-containing dyestuffs. However, in dyed products thereby obtained, the dyestuffs are fixed to fibers by ionic bond and there has been a general tendency that the washing fastness is low. It is also known to dye such fibers by means of reactive dyestuffs. In this case, however, the dyeing properties tend to be inadequate although the washing fastness may be satisfactory, and such a method is not practically employed very much.

On the other hand, reflecting diversification of fibers in recent years, there have been many cases in which nylon or polyurethane fibers are used in combination with polyester or triacetate fibers in the form of a fiber mixture. However, the above mentioned acid dyestuffs, metal-containing dyestuffs and reactive dyestuffs are all water-soluble dyestuffs and as such, unable to dye polyester or triacetate fibers.

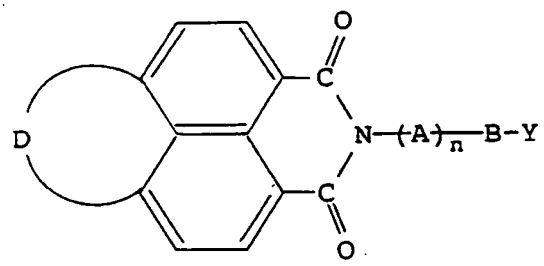
In recent years, dyestuffs having fluorescence are desired. However, there have been few dyestuffs which are capable of dyeing nylon or polyurethane fibers with fluorescent colors.

Under these circumstances, the present inventors have conducted various studies with an aim to obtain dyestuffs which are capable of dyeing nitrogen-containing fibers such as nylon or polyurethane and polyester or triacetate fibers simultaneously and which provides dyed products having excellent washing fastness. As a result, they have found that dyestuffs having a water-insoluble compound composed of a certain specific naphthalic acid imide derivative as the matrix and-having a certain specific 6-membered heterocyclic ring with at least one active halogen atom bonded thereto, are capable of dyeing both fibers and yet capable of providing dyed products having excellent fastness and fluorescent greenish yellow or orange colors.

Document DE-B-1569761 describes naphthalic acid imide dyestuffs with no fiber reactive group (see examples 4 and 10) for the dyeing of polyester.

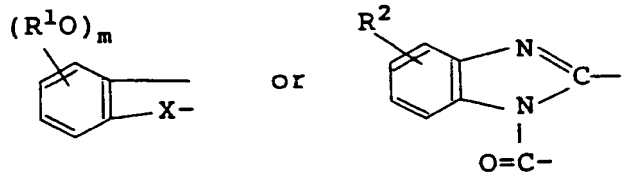
Document FR-A-2144737 shows reactive group and water solubilizing groups HSO_3 bearing naphthalic acid imide dyestuffs for dyeing of PA and PU (see examples 32 - 34 in connection with claim 11).

The present invention provides water-insoluble naphthalic acid imide dyestuffs of the following formula:



(I)

wherein D is



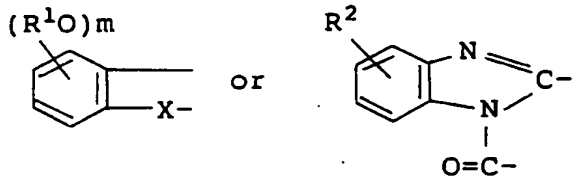
wherein R^1 is C_1-C_8 alkyl which may be substituted, R^2 is hydrogen, halogen, lower alkyl, lower alkoxy or cyano, X is oxygen or sulfur, and m is 0 or 1; A is phenylene, alkylene, aralkylene or $-C_2H_4OC_2H_4-$; B is oxygen, sulfur or

wherein R^3 is hydrogen or lower alkyl; Y is a triazine, pyrimidine or pyridazine ring having at least one active halogen atom; and n is 0 or 1.

Now, the present invention will be described in detail with reference to the preferred embodiments.

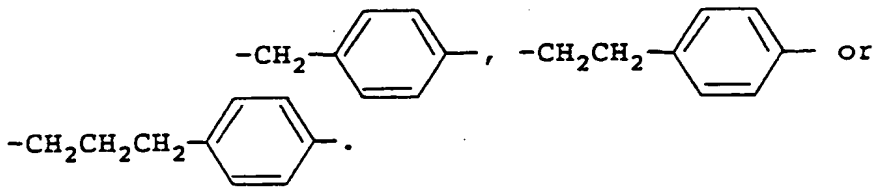
The dyestuffs of the present invention are basically water-insoluble and of the same kind as disperse dyestuffs which have been used for polyester fibers. However, the dyestuffs of the present invention further have reactive groups in their structures, which are reactive with nitrogen-containing fibers. Thus, the dyestuffs of the present invention belong to the category of so-called "reactive disperse dyestuffs".

In the above formula (I), D is a substituent of the formula:



In this substituent, the C_1-C_8 alkyl for R^1 may, for example, be methyl, ethyl, straight chain or branched chain propyl, butyl, pentyl, hexyl, heptyl or octyl. Particularly preferred is C_1-C_3 alkyl. Such alkyl may be a substituted alkyl, for example, C_1-C_4 alkoxy C_1-C_4 alkyl such as metoxyethyl, ethoxyethyl, butoxyethyl or butoxypropyl, or hydroxy C_1-C_4 alkyl such as hydroxyethyl or hydroxybutyl. However, non-substituted alkyl is preferred. X is oxygen or sulfur. Particularly preferred is oxygen. Further, m is 0 or 1. Particularly preferred is 1. R^2 is hydrogen, halogen, lower alkyl, lower alkoxy or cyano. Here, the halogen may usually be fluorine, chlorine or bromine. Particularly preferred is chlorine. The carbon number of the lower alkyl and lower alkoxy for R^2 is usually from 1 to 4. Among them, methyl and methoxy are preferred. With respect to the position at which the substituent R^2 is introduced, it is usually impossible to introduce the substituent at a predetermined single position in view of the synthesis of the compound. Therefore, when R^2 is other than hydrogen, the compound of the present invention is usually a mixture of isomers having R^2 introduced at different positions.

A is phenylene, alkylene, aralkylene or $-C_2H_4OC_2H_4-$. The alkylene for A may usually be a straight chain or branched chain alkylene group such as methylene, ethylnene, n-propylene, iso-propylene, iso-butylene, n-butylene or n-hexylene. Particularly preferred among them is C_1-C_3 alkylene. The aralkylene for A may, for example, be

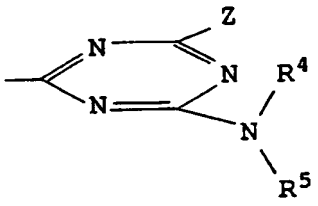


Particularly preferred as A is alkylene. Further, n is 0 or 1. Particularly preferred is 1.

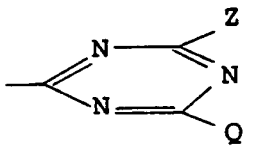
B is oxygen, sulfur or

wherein R^3 is hydrogen, or C_1-C_4 lower alkyl such as methyl, ethyl or propyl. Particularly preferred as B is oxygen.

Y is a 6-membered nitrogen-containing heterocyclic ring having at least one active halogen atom. This heterocyclic ring is preferably a heterocyclic ring having 2 or 3 nitrogen atoms such as triazine, pyrimidine or pyridazine. The active halogen atoms include fluorine, chlorine and bromine. There is no particular restriction as to the number of such halogen atoms. However, it is usually preferred that one or two chlorine or fluorine atoms are directly substituted on the heterocyclic ring. Further, the heterocyclic ring may have a substituent other than the active halogen atoms, such as C_1-C_4 alkyl, C_1-C_4 alkoxy, amino which may be substituted, cyano, C_1-C_4 alkyl sulfonyl or morpholino. The substituent for the substituted amino may be alkyl, alkoxyalkyl, alkoxyalkoxyalkyl, alkenyl, aryl or aralkyl. Specific examples of Y wherein the nitrogen-containing heterocyclic ring is a triazine ring, include those represented by the following formulas:



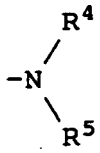
and



In the above formulas, Z is halogen such as fluorine, chlorine or bromine. Particularly preferred is fluorine or chlorine. Each of R^4 and R^5 which are independent from each other, is hydrogen, alkyl which may be substituted by cyano, hydroxyl, lower alkoxy, lower alkoxy lower alkoxy or dialkylamino, alkenyl, cyclohexyl, aryl or aralkyl or $-NR^4R^5$ represents a 5-memberd or 6-membered nitrogen-containing heterocyclic ring formed by the linkage of R^4 and R^5, provided that the total number of carbon atoms of R^4 and R^5 is not higher than 18.

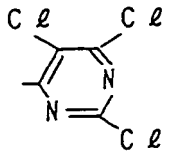
Q may be the same halogen as Z, lower alkyl such as methyl or ethyl, phenyl, lower alkyl sulfonyl such as methyl sulfonyl, $-OR^6$ or $-SR^6$ wherein R^6 is lower alkyl such as methyl or ethyl, lower alkoxy lower alkoxy such as ethoxyethoxy, or phenyl.

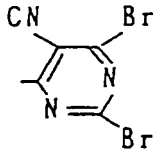
The alkyl for R^4 and R^5 is preferably C_1-C_8 unsubstituted alkyl such as methyl, ethyl, straight chain or branched chain propyl, butyl, pentyl, hexyl, heptyl, or octyl, or C_1-C_8 alkyl substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy such as 3-methoxypropyl, ethoxyethyl, 3-ethoxypropyl, 3-propoxypropyl, 3-isopropoxypropyl, 3-butoxypropyl, butoxyethyl, 3-isobutoxypropyl, methoxyethoxyethyl or ethoxypropoxypropyl. The alkenyl may be C_3-C_4 alkenyl such as allyl. The aryl may be phenyl. The aralkyl may be benzyl or phenethyl. The

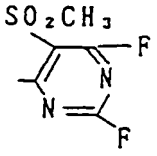


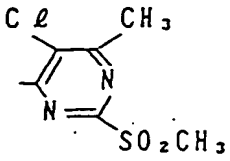
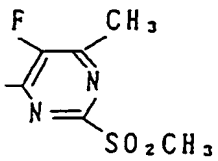
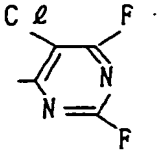
is preferably monoalkyl amino substituted by C_1-C_4 lower alkoxy.

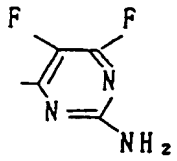
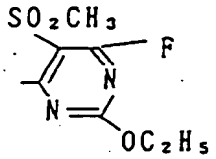
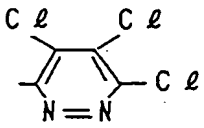
Specific examples of Y wherein the nitrogen-containing heterocyclic ring is a pyrimidine ring or a pyridazine ring, include those represented by the following formulas:



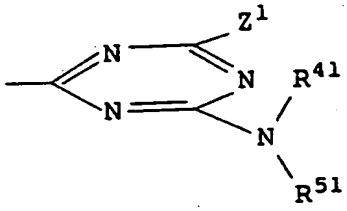




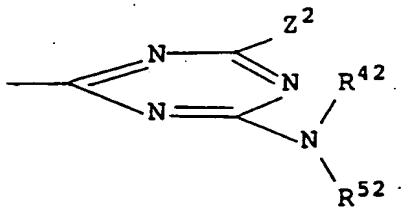




The 6-membered nitrogen-containing heterocyclic ring having at least one active halogen atom represented by Y is preferably the one wherein the heterocyclic ring is a triazine ring. Preferred as Y is the following substituent:



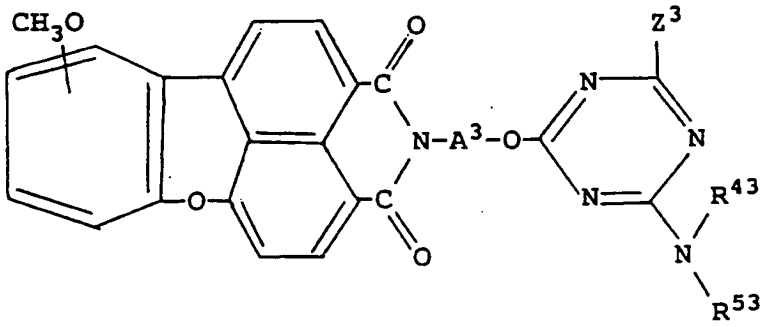
wherein Z^1 is fluorine or chlorine, and each of R^{41} an R^{51} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy, alkenyl, aryl or aralkyl or $-NR^{41}R^{51}$ is a 6-membered nitrogen-containing heterocyclic ring formed by the linkage of R^{41} and R^{51}.

Further, particularly preferred as Y is the following substituent:



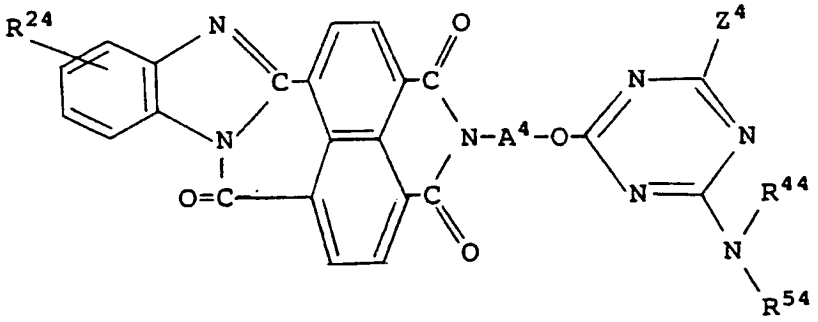
wherein Z^2 is fluorine or chlorine, and each of R^{42} and R^{52} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy.

Among the dyestuffs of the above formula (I) of the present invention, particularly preferred are dyestuffs of the following formula (I-1) or (I-2):



(I-1)

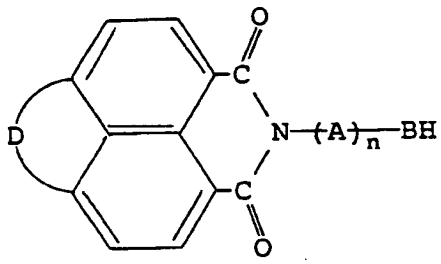
wherein A^3 is C_1-C_3 alkylene or aralkylene, Z^3 is fluorine or chlorine, and each of R^{43} and R^{53} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy.



(I-2)

wherein A^4 is C_1-C_3 alkylene or aralkylene, R^{24} is chlorine, methyl or methoxy, Z^4 is fluorine or chlorine, and each of R^{44} and R^{54} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy.

The dyestuff of the formula (I) can readily be prepared by reacting a water-insoluble compound of the following formula (a):



(a)

wherein D, A, B and n are as defined in the formula (I), with a heterocyclic compound of the following formula (b):

Hal-Y (b)

wherein Hal is an active halogen atom, and Y is as defined above with respect to the formula (I). This reaction can be conducted by heating the compound of the formula (a) with from 1 to 1.2 molar times, relative to the compound of the formula (a), of the heterocyclic compound of the formula (b) in an organic solvent such as acetone, methyl ethyl ketone, toluene, nitrobenzene, dioxane, N,N-dimethylformamide, N-

methyl-2-pyrrolidone or dimethylsulfoxide in the presence of from 1 to 2 molar times, relative to the compound of the formula (a), of an acid binder, for example, a tertiary amine such as triethylamine, tributylamine or N,N-diethylaniline, or an inorganic base such as potassium carbonate or potassium hydrogen carbonate, at a temperature of from 0 to 90 °C for from 0.5 to 5 hours. The resulting reaction solution is cooled and then put into water, whereupon the resulting precipitate is separated by a suitable method such as filtration or centrifugal separation to obtain a dyestuff of the formula (I) of the present invention substantially quantitatively.

The water-insoluble reactive dyestuff of the present invention are capable of dyeing not only nitrogen-containing fibers such as polyurethane fibers and polyamide fibers including nylon, silk and wool, but also polyester fibers and triacetate fibers. Accordingly, it is particularly suitable for use for dyeing a fiber mixture comprising (1) polyamide or polyurethane fibers and (2) polyester or triacetate fibers, which used to be very difficult to dye simultaneously. Further, the dyestuffs of the present invention are useful for dyeing almost all other fibers including cellulose fibers, viscous rayon, hemp, silk, and wool.

Further, the dyestuffs of the present invention are useful not only as dyes for dyeing fibers or fabrics but also as colorants-for coloring paper or synthetic resins, or as coloring matters for an ink for an ink jet printer.

To carry out the dyeing by means of the dyestuff of the present invention, it is desirable to finely disperse the dyestuff of the formula (I) in a medium in a particle size of from 0.5 to 2 μm. This can be done by:

(1) a method of finely dispersing it in water by means of a pulverizer such as a sand grinder using a water-soluble dispersing agent such as a pluronic type non-ionic surfactant or an anionic dispersing agent such as sodium ligninsulfonate or a sodium salt of a naphthalene sulfonic acid-formaline condensation product;

(2) a method of finely dispersing it in an organic solvent such as an alcohol, a ketone, a hydrocarbon, a haloganated hydrocarbon, an ester, an ether or a mixture thereof, using a sulfosuccinic acid ester or a compound obtained by adding a small molar amount of ethylene oxide to e.g. nonyl phenol; or

(3) a method of finely dispersing it in a mixture comprising water and a solvent selected from the above mentioned solvents, which can optionally be mixed with water.

Further, during the process of finely dispersing the dyestuff as mentioned above, a polymer compound soluble in the respective dispersing medium or a surfactant or the like having a function other than the dispersing function, may also be incorporated.

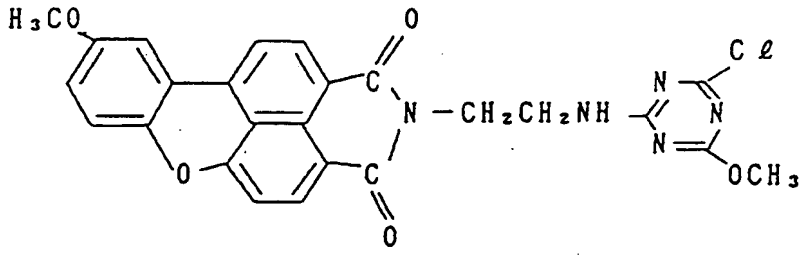
As a method for dyeing fibers by means of this finely dispersed dye solution, a dip dyeing method, a padding dyeing method or a printing method may usually be employed. The dyeing conditions vary depending upon the fibers to be treated, but may usually be the conditions commonly employed for dyeing the respective fibers. For example, in a case where a fiber mixture of polyester and nylon is to be dyed by a dip dyeing method, the pH of the dye bath is from 5 to 7, and the temperature for dyeing is at a level of from 120 to 130 °C. On the other hand, when cellulose fibers are to be dyed by a padding method, from 6 to 12%, based on the padding bath, of a cellulose fiber swelling agent is added to the padding bath, the pH of the bath is adjusted to a level of form 7 to 9, and the temperature for dyeing is adjusted to a level of from 120-220 °C. Further, treatment after the dyeing may be conducted in accordance with a usual method, which includes soaping, washing with water and drying.

The dyestuffs of the present invention are capable of simultaneously dyeing polyester or triacetate fibers and nitrogen-containing fibers, and yet the resulting dyed products have fluorescent clear colors and being excellent in the washing fastness. Thus, it is very useful.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

Example 1

A mixture comprising 25 g of a dyestuff of the following structural formula:



438 nm

(solvent: dimethylformamide (hereinafter referred to as DMF))

25 g of a naphthalene sulfonic acid-formaldehyde condensation product and 50 mℓ of water, was finely dispersed by means of a sand grinder as a finely dispersing machine, to obtain a dye dispersion. Using this dye dispersion, a dye bath (pH 5.1) having the following composition:

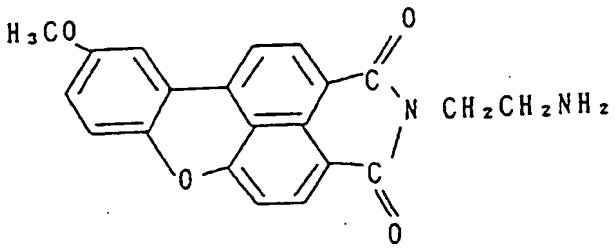
Dye dispersion	1.5 g
Water	Rest
	200 mℓ

was prepared, and 10 g of a fine denier polyester/nylon blend cloth (blending ratio: 8/2) was dipped into the dye bath and gradually heated from room temperature to 130 °C and dyed at 130 ° for one hour.

Then, washing was conducted at 80 °C for 10 minutes at a bath ratio of 1:50 using a washing solution comprising 2 g/ℓ of each of a nonionic surfactant (Diaserver® SC-CT 40, manufactured by Mitsubishi Kasei Corporation), sodium hydroxide and hydrosulfite, to obtain a dyed product having a fluorescent greenish yellow color. The obtained dyed product had a light-fastness of 4-5 grade (JIS L-0842, 20 hours), a washing fastness of 4-5 grade (JIS L-844 Method A-2, stain to a nylon white cloth), and a water-fastness of 4-5 grade (JIS L-846 Method A, stain to a nylon white cloth) and thus was excellent in these properties.

The dyestuff used in this-Example was prepared as follows:

3.3 g of a dyestuff of the following structural formula:

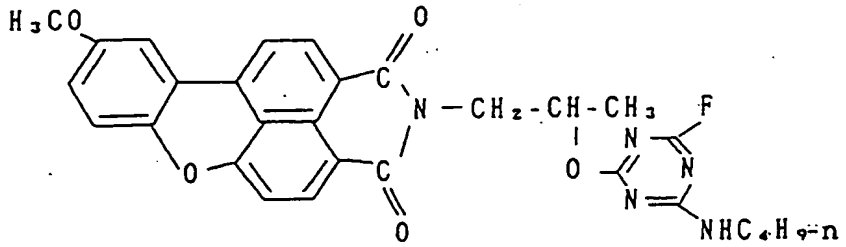


was dissolved in 50 mℓ of N-methyl-2-pyrrolidone, and 2.0 g of 2,4-dichloromethoxy-s-tiazine and 2.0 g of triethylamine were added thereto. The mixture was reacted at 40 °C for 2 hours. The reaction mixture was put into 1 ℓ of iced water, and precipitated crystals were collected by filtration, washed with water and dried

to obtain 4.4 g of yellow crystals. This dyestuff had λ_{max} (DMF) at 438 nm.

Example 2

A mixture comprising 250 g of a dyestuff of the following formula:



λ_{max} 438 nm

(Solvent: DMF)

250 g of a naphthalene sulfonic acid-formaldehyde condensation product and 500 mℓ of water, was finely dispersed by means of a sand grinder as a finely dispersing machine, to obtain a dye dispersion.

Using this dye dispersion, a padding bath having the following composition:

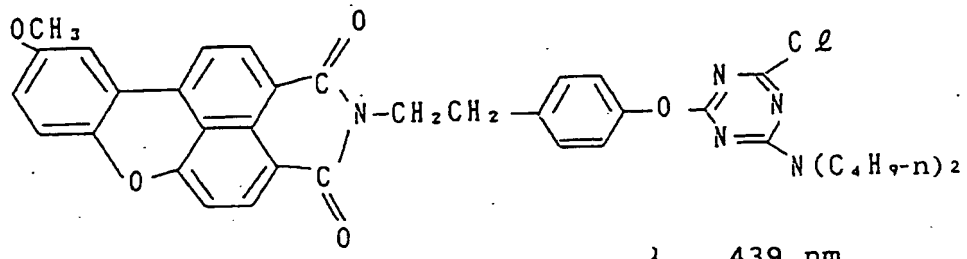
Dye dispersion	50 g
Sodium acetate	5 g
Water	Rest
	1,000 g

was prepared, and a triacetate/nylon blend cloth was dipped in the bath, then squeezed at a squeezing rate of 65%, dried at 100 °C for 2 minutes, fixed at 180 °C for 7 minutes by a H. T. S. machine, followed by washing in the same manner as described in Example 1, to obtain a dyed cloth having a fluorescent greenish yellow color.

This dyed product had a light-fastness of 4 grade (JIS L-0842, 20 hours), a washing fastness of 4-5 grade (JIS L-844 Method A-2, stain to a nylon white cloth) and a water fastness of 4-5 grade (JIS L-846 Method of A, stain to a nylon white cloth) and thus was excellent in these properties.

Example 3

A mixture comprising 25 g of a dyestuff of the following formula:



λ_{max} 439 nm

(Solvent: DMF)

6 g of a nonionic dispersing agent (Newcol 710F, manufactured by Nippon Nyukazai K.K.), 4 g of a lignin sulfonic acid type anion dispersing agent (Reax 85 A, manufactured by West Veco), 5 g of propylene glycol and 60 mℓ of water, was finely dispersed by means of a paint shaker as a finely dispersing machine, to obtain a dye dispersion.

Using this dispersion, a printing paste (pH 7.0) having the following composition:

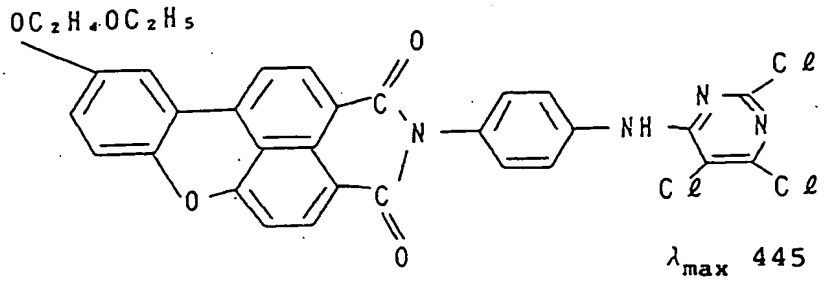
Dye dispersion	80 g
O/W emulsion having sodium alginate as the base	600 g
Sodium polyphosphate	5 g
Water	Rest
	1,000 g

was prepared, and a polyester/polyurethane blend cloth (blending ratio: 8/2) was subjected to screen printing by means of a screen printing machine, then subjected to intermediate drying at 80 °C for 3 minutes and thereafter fixed at 130 °C for 20 minutes by a H. P. S. machine. Then, washing was conducted in the same manner as described in Example 1 to obtain a printed cloth having a fluorescent greenish yellow color.

This printed cloth had a light-fastness of 4-5 grade (JIS L-0842, 20 hours), a washing fastness of 5^{-} grade (JIS L-844 Method A-2, stain to a nylon white cloth) and a water fastness of 4 grade (JIS L-846 Method A, stain to a nylon white cloth) and thus was excellent in these properties.

Example 4

A mixture comprising 25 g of a dyestuff of the following formula:



λ_{max} 445 nm

(Solvent: DMF)

25 g of a naphthalene sulfonic acid-formaldehyde condensation product and 50 mℓ of water, was finely dispersed by means of a sand grinder as a finely pulverizing machine, to obtain a dye dispersion.

Using this dye dispersion, a dye bath (pH 5.0) having the following composition:

Dye dispersion	1.5 g
p-Phenylphenol (used as a carrier)	1.0 g
Water	Rest
	200 mℓ

was prepared, and 10 g of a polyester/triacetate/wool blend cloth (blending ratio: 5/3/2) was dipped in the dye bath, then gradually heated from room temperature to 125°C and dyed at this temperature for one hour.

Then, the dyed cloth was washed with water and then washed at a bath ratio of 1:50 using a washing solution containing 2 g/ℓ of a nonionic surfactant (Diaserver® SC-CT40, manufactured by Mitsubishi Kasei Corporation), to obtain a dyed product having a uniform fluorescent greenish yellow color.

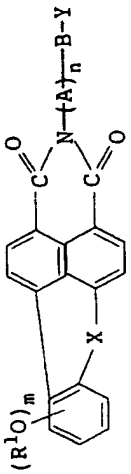
This dyed cloth had a light-fastness of 4 grade (JIS L-0842, 20 hours) and a washing fastness of 5⁻ grade (JIS L-844 Method A-2, stain to a wool white cloth) and thus was excellent in these properties.

Example 5

A fine denier polyester/nylon blend cloth (blending ratio: 8/2) was dyed by means of a dyestuff as identified in the following Table 1 in accordance with Example 1, to obtain a dyed cloth having a color as identified in the same Table.

Each dyed product thereby obtained had excellent light fastness of at least 4 grade, and the washing fastness (stain to a nylon white cloth) was excellent at level of at least 4 grade.

Table 1



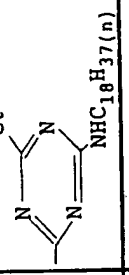
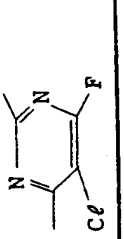
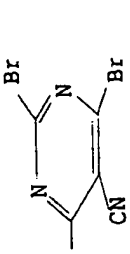
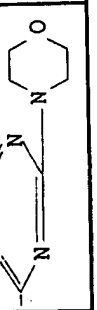
NO.	$(R^1O)_m$	-X-	$-(A)_n-$	-B-	-Y	λ_{max} (solvent: DMF) nm	Color
5-1	H_5C_2O	-O-	—	-NH-		436	Fluorescent greenish yellow
5-2	H_7C_3O (n)	-O-	$-CH_2-CH-CH_3$	-O-		438	Fluorescent greenish yellow
5-3	H_3CO	-O-	$-C_4H_8-$	-O-		440	Fluorescent greenish yellow
5-4	H_3CO	-O-	$-C_2H_4-$	CH_3 | -N-		439	Fluorescent greenish yellow

Table 1 (continued)

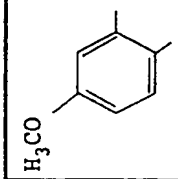
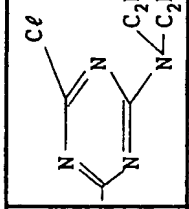
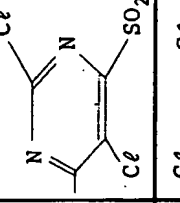
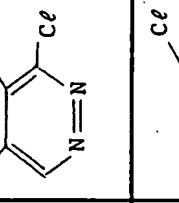
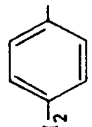
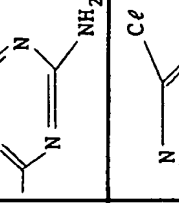
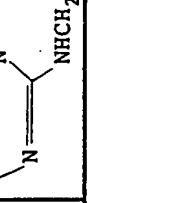
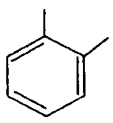
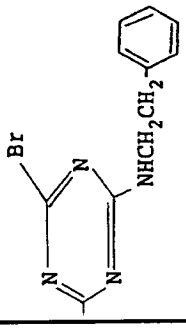
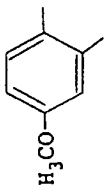
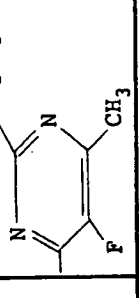
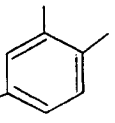
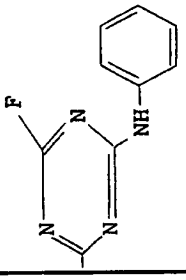
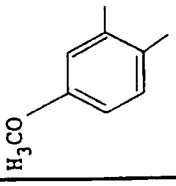
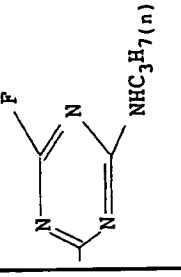
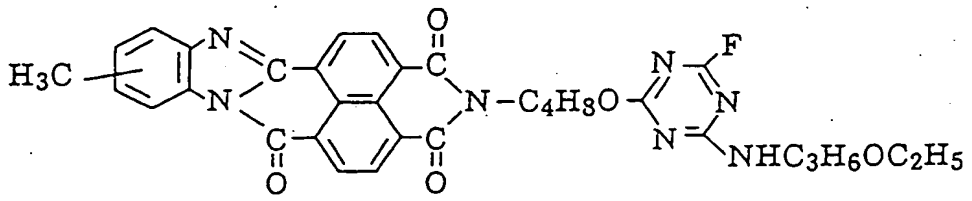
5-5		-O-	$-CH_2CH_2CHCH_3$ |	-O-		438	Fluorescent greenish yellow
5-6		-O-	$-C_3H_6-$	-NH-		439	Fluorescent greenish yellow
5-7		-O-	$-C_2H_4-$	$C_3H_{7(n)}$ | -N-		438	Fluorescent greenish yellow
5-8		-S-		-NH-		448	Fluorescent greenish yellow
5-9		-O-	$-C_3H_6-$	-O-		438	Fluorescent greenish yellow

Table 1 (continued)

5-10		-S-	$-C_4H_8-$	-O-		440	Fluorescent greenish yellow
5-11		-S-	$-CH_2-$	-O-		427	Fluorescent greenish yellow
5-12		-O-	$-C_5H_{10}-$	-O-		438	Fluorescent greenish yellow
5-13		-O-	$-C_2H_4OC_2H_4-$	-O-		435	Fluorescent greenish yellow

Example 6

A mixture comprising 25 g of a dyestuff of the following structural formula:



25 g of a naphthalene sulfonic acid-formaldehyde condensation product and 50 mℓ of water, was finely pulverized by means of a sand grinder as a finely dispersing machine, to obtain a dye dispersion.

Using this dye dispersion, a dye bath (pH 5.1) having the following composition:

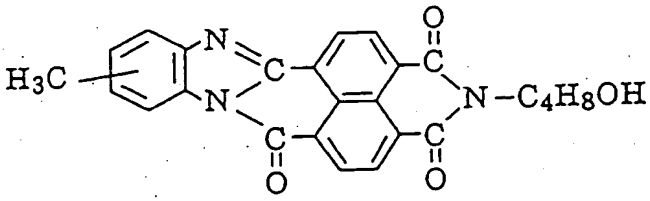
Dye dispersion	1.5 g
Water	Rest
	200 mℓ

was prepared, and 10 g of a fine denier polyester/nylon blend cloth (blending ratio: 8/2) was dipped in the dye bath, then gradually heated from room temperature to 130 °C and dyed at that temperature for one hour.

Then, washing was conducted at 80 °C for 10 minutes at a bath ratio of 1:50 using a washing solution containing 2 g/ℓ of each of a nonionic surfactant (Diaserver® SC-CT 40, manufactured by Mitsubishi Kasei Corporation), sodium hydroxide and hydrosulfite, to obtain a dyed product having a fluorescent orange color. This dyed product had a washing fastness of 4-5 grade (JIS L-844 Method A-2, stain to a nylon white cloth) and a water fastness of 4-5 grade (JIS L-846 Method A, stain to a nylon white cloth) and thus was excellent in these properties.

The dyestuff used in this Example was prepared as follows:

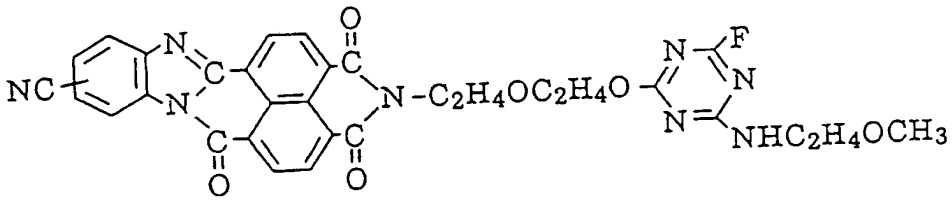
5.9 g of a dyestuff of the following naphthalic acid imide compound:



was dissolved in 80 mℓ of N-methyl-2-pyrrolidone, and the solution was cooled to -5 °C. Then, 1.4 g of trifluorotriazine was gradually added thereto, and the mixture was stirred for 30 minutes. Then, 1.0 g of triethylamine was added thereto, and the mixture was stirred at a temperature of from -5 °C to 0 °C for 2 hours. Further, 1.0 g of ethoxypropylamine was added thereto at the same temperature and reacted for 30 minutes. After completion of the reaction, the reaction product was put into 1 ℓ of ice water. Precipitated crystals were collected by filtration, washed with water and dried to obtain 7.5 g of orange color crystals. This dyestuff had λ_{max} (solvent: acetone) at 431nm.

Example 7

A mixture comprising 250 g of a dyestuff of the following formula:



λ_{max} (solvent: acetone) 416 nm

250 g of a naphthalenesulfonic acid-formaldehyde condensation product and 500 mℓ of water, was finely dispersed by means of a sand grinder as a finely dispersing machine, to obtain a dye dispersion.

Using this dye dispersion, a padding bath having the following composition:

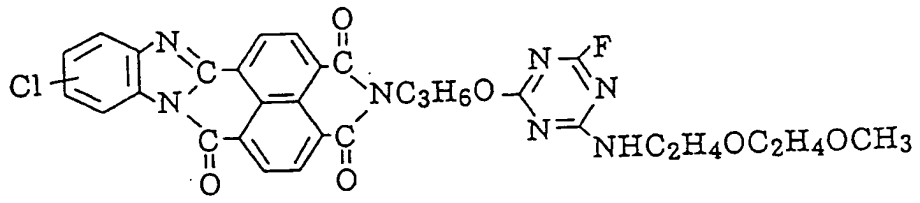
Dye dispersion	50 g
Sodium acetate	5 g
Water	Rest
	1,000 g

was prepared, and a triacetate/nylon blend cloth was dipped in the bath, then squeezed at a squeezing rate of 65%, dried at 100°C for 2 minutes, fixed at 180°C for 7 minutes by a H. T. S. machine, followed by washing in the same manner as described in Example 6, to obtain a dyed cloth having a fluorescent greenish yellow color.

The washing fastness (JIS L-844 Method A-2, stain to a nylon white cloth) of this dyed product was excellent at a level of 4-5 grade. Further, the water fastness (JIS L-846 Method A, stain to a nylon white cloth) was also excellent at a level of 4-5 grade.

Example 8

A mixture comprising 25 g of a dyestuff of the following formula:



λ_{max} (solvent: acetone) 420 nm

6 g of a nonionic dispersing agent (Newcol 710F, manufactured by Nippon NyukaZai K.K.), 4 g of a lignin sulfonic acid type anion dispersing agent (Reax 85 A, manufactured by West Veco), 5 g of propylene glycol and 60 mℓ of water, was finely dispersed by means of a paint shaker as a finely dispersing machine, to obtain a dye dispersion.

Using this dispersion, a printing paste (pH 7.0) having the following composition:

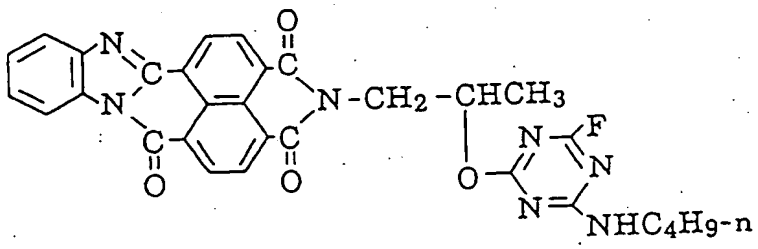
Dye dispersion	80 g
O/W emulsion having sodium alginate as the base	600 g
Water	Rest
	1,000 g

was prepared, and a polyester/polyurethane blend cloth (blending ratio: 8/2) was subjected to screen printing by means of a screen printing machine, then subjected to intermediate drying at 100 °C for 3 minutes and thereafter fixed at 130 °C for 20 minutes by a H. P. S machine. Then, washing was conducted in the same manner as described in Example 6 to obtain a printed cloth having a fluorescent yellow color.

The washing fastness (JIS L-844 Method A-2, stain to a nylon white cloth) of this dyed cloth was excellent at a level of 4-5 grade.

Example 9

A mixture comprising 25 g of a dyestuff of the following formula:



λ_{max} (solvent: acetone) 430 nm

25 of a naphthalene sulfonic acid-formaldehyde condensation product and 50 mℓ of water, was finely dispersed by means of a sand grinder as a finely pulverizing machine, to obtain a dye dispersion.

Using this dye dispersion, a dye bath (pH 5.0) having the following composition:

Dye dispersion	1.5 g
p-Phenylphenol (used as a carrier)	1.0 g
Water	Rest
	200 mℓ

was prepared, and 10 g of a polyester/triacetate/wool blend cloth (blending ratio: 5/3/2) was dipped in the dye bath, then gradually heated from room temperature to 125 °C and dyed at this temperature for one hour.

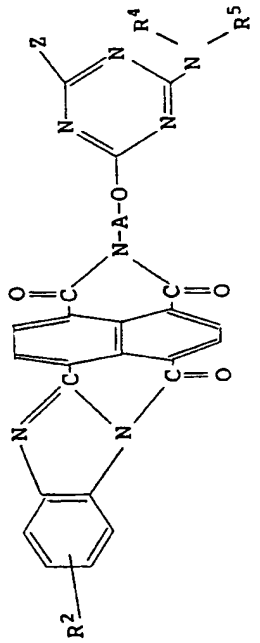
Then, the dyed cloth was washed with water and then washed at a bath ratio of 1:50 using a washing solution containing 2 g/ℓ of a nonionic surfactant (Diaserver® SC-CT40, manufactured by Mitsubishi Kasei Corporation), to obtain a dyed product having a fluorescent orange color.

The washing fastness (JIS-L-844 Method A-2, stain to a wool white cloth) of this dyed product was excellent at a level of 5 grade.

Example 10

A fine denier polyester/nylon blend cloth (blending ratio: 8/2) was dyed by means of a dyestuff as identified in Table 2 in accordance with Example 6, to obtain a dyed cloth having a color as identified in Table 2. The washing fastness (JIS L-844 Method A-2, stain to a nylon white cloth) of each dyed product was excellent at a level of at least 4 grade.

Table 2

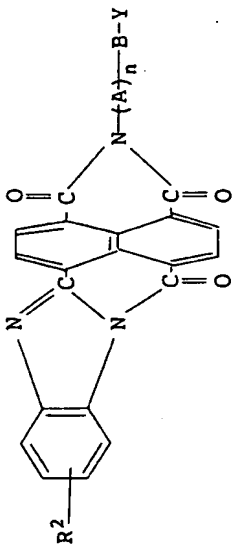


No.	$-R^2$	-A-	-Z	$-N\begin{matrix}R^4\\R^5\end{matrix}$	λ_{max} (solvent: acetone) nm	Color
10-1	$-C_4H_{9(n)}$	$-C_2H_4-$	-F	$-NHC_6H_{13(sec)}$	435	Fluorescent orange
10-2	$-CH_3$	$-C_6H_{12}-$	-F	$-NHC_3H_6OC_3H_{7(i)}$	436	Fluorescent orange
10-3	-Br	$-C_4H_8-$	-Cℓ	$-NHC_8H_{17(n)}$	421	Fluorescent yellow
10-4	$-OCH_3$	$-C_2H_4OC_2H_4-$	-F	$-N\begin{matrix}C_2H_4OC_2H_5\\C_2H_4OC_2H_5\end{matrix}$	448	Fluorescent orange
10-5	$-CH_3$	$-C_2H_4OC_2H_4-$	-F	$-NHC_2H_4OC_4H_{9(n)}$	432	Fluorescent orange
10-6	$-C_2H_5$	$-C_3H_6-$	-Br	$-N\begin{matrix}CH_3\\CH_3\end{matrix}$	434	Fluorescent orange

Example 11

A fine denier polyester/nylon blend cloth (blending ratio: 8/2) was dyed by means of a dyestuff as identified in Table 3 in accordance with Example 6, to obtain a dyed cloth having a color as identified in Table 3. The washing fastness (JIS L-844 Method A-2, stain to a nylon white cloth) of each dyed product thus obtained was excellent at a level of at least 4 grade.

Table 3



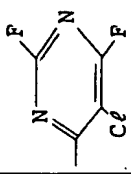
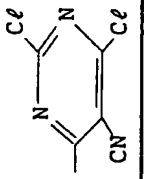
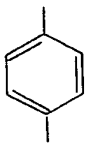
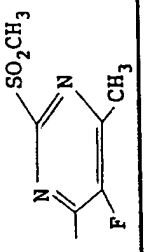
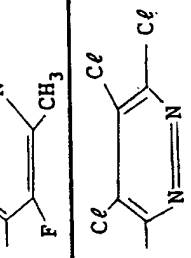
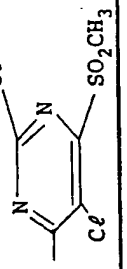
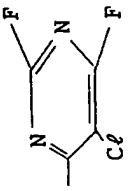
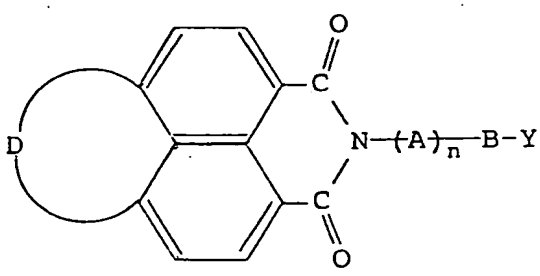
NO.	$-R^2$	$-(A)_n-$	-B-	-Y	λ_{max} (solvent: DMF) nm	Color
11-1	$-CH_3$	$-C_2H_4-$	-O-		434	Fluorescent orange
11-2	-Br	$-C_3H_6-$	-O-		420	Fluorescent yellow

Table 3 (continued)

11-3	$-C_4H_{9(n)}$		-O-		429	Fluorescent orange
11-4	$-C_2H_5$	$-C_4H_8-$	CH_3 | -N-		430	Fluorescent orange
11-5	$-OCH_3$	$-C_2H_4-$	-S-		445	Fluorescent orange
11-6	-CN	$-C_2H_4OC_2H_4-$	-O-		413	Fluorescent yellow

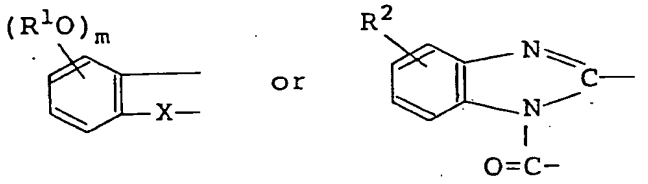
Claims

1. Water-insoluble naphthalic acid imide dyestuffs of the following formula:



(I)

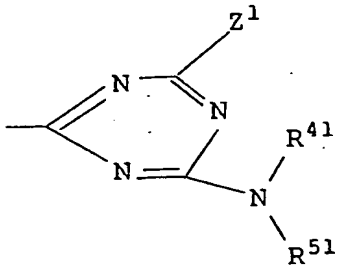
wherein D is



wherein R^1 is C_1-C_8 alkyl which may be substituted, R^2 is hydrogen, halogen, lower alkyl, lower alkoxy or cyano, X is oxygen or sulfur, and m is 0 or 1; A is phenylene, alkylene, aralkylene or $-C_2H_4OC_2H_4-$; B is oxygen, sulfur or

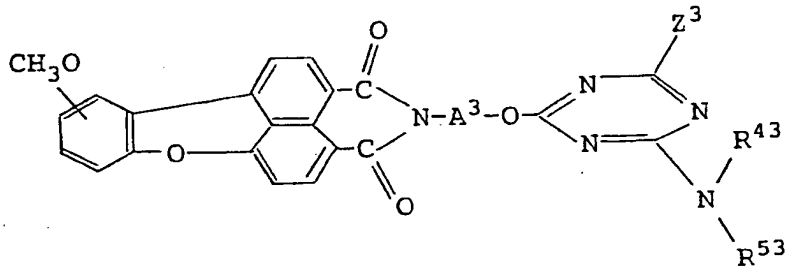
wherein R^3 is hydrogen or lower alkyl ; Y is a triazine, pyrimidine or pyridazine ring having at least one active halogen atom; and n is 0 or 1.

2. The dyestuffs according to Claim 1, wherein Y is a substituent of the following formula:



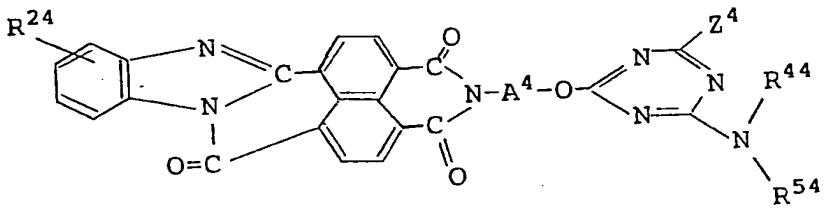
wherein Z^1 is fluorine or chlorine, each of R^{41} and R^{51} which are independent from each other, is hydrogen, C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy, alkenyl, aryl or aralkyl, or $-NR^{41}R^{51}$ represents a 6-membered nitrogen-containing heterocyclic ring formed by the linkage of R^{41} and R^{51}.

3. The dyestuffs according to Claim 1, which are represented by the following formula:



wherein A^3 is a C_1-C_3 alkylene or aralkylene; Z^3 is fluorine or chlorine; and each of R^{43} and R^{53} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy.

4. The dyestuffs according to Claim 1, which are represented by the following formula:

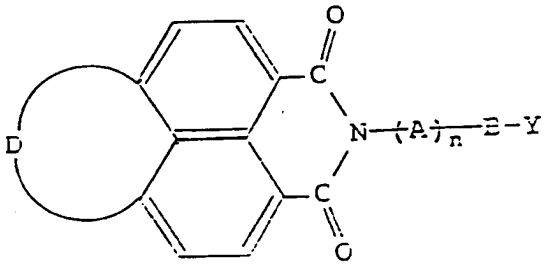


wherein A^4 is C_1-C_3 alkylene or aralkylene; R^{24} is chlorine, methyl or methoxy; Z is fluorine or chlorine; and each of R^{44} and R^{54} which are independent from each other, is hydrogen, or C_1-C_8 alkyl which may be substituted by C_1-C_4 alkoxy or C_1-C_4 alkoxy C_1-C_4 alkoxy.

5. The dyestuffs according to Claim 1, which are dyestuffs for dying a fiber mixture comprising (1) polyamide or polyurethane fibers and (2) polyester or triacetate fibers.

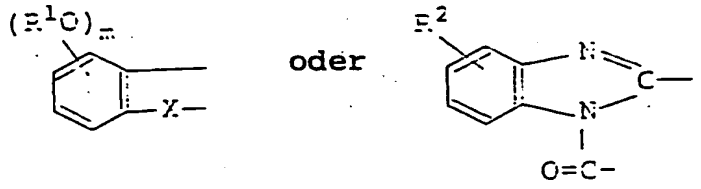
Patentansprüche

1. Wasserunlösliche Naphthalimidfarbstoffe der folgenden Formel:

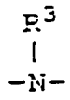


(I)

worin D

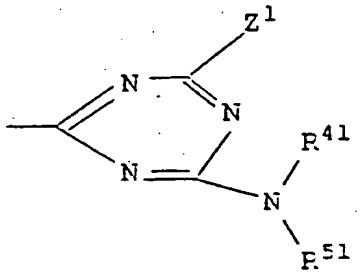


ist, wobei R^1 C_1-C_8-Alkyl ist, das substituiert sein kann, R^2 Wasserstoff, Halogen, niederes Alkyl, niederes Alkoxy oder Cyano ist, X Sauerstoff oder Schwefel ist, und m 0 oder 1 ist; A Phenylen, Alkylen, Aralkylen oder $C_2H_4OC_2H_4$-ist; B Sauerstoff, Schwefel oder



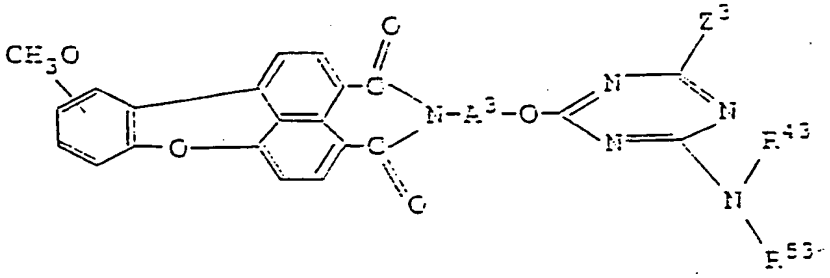
ist, wobei R^3 Wasserstoff oder niederes Alkyl ist; Y ein Triazin-, Pyrimidin- oder Pyridazinring mit mindestens einem aktiven Halogenatom ist; und n 0 oder 1 ist.

2. Farbstoffe gemäß Anspruch 1, wobei Y ein Substituent der folgenden Formel ist:



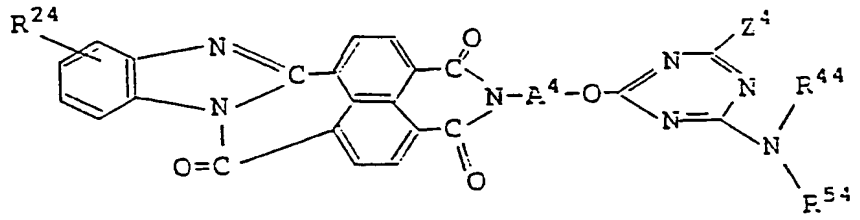
wobei Z^1 Fluor oder Chlor ist, R^{41} und R^{51} jeweils unabhängig voneinander Wasserstoff oder C_1-C_8-Alkyl ist, das substituiert sein kann durch C_1-C_4-Alkoxy oder C_1-C_4-Alkoxy-C_1-C_4-Alkoxy, Alkenyl, Aryl oder Aralkyl oder $-NR^{41}R^{51}$ stellt einen 6-gliedrigen stickstoffenthaltenden heterocyclischen Ring dar, gebildet durch die Verbindung von R^{41} und R^{51}.

3. Farbstoffe gemäß Anspruch 1, die durch die folgende Formel dargestellt sind:



wobei A^3 ein C_1-C_3-Alkylen oder Aralkylen ist; Z^3 Fluor oder Chlor ist; und R^{43} und R^{53} jeweils unabhängig voneinander Wasserstoff oder C_1-C_8-Alkyl ist, das substituiert sein kann durch C_1-C_4-Alkoxy oder C_1-C_4-Alkoxy-C_1-C_4-Alkoxy.

4. Farbstoffe gemäß Anspruch 1, die dargestellt werden durch die folgende Formel:

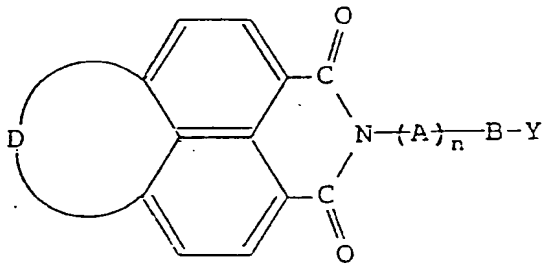


wobei A^4 C_1-C_3-Alkylen oder Aralkylen ist; R^{24} Chlor, Methyl oder Methoxy ist; Z^4 Fluor oder Chlor ist; und R^{44} und R^{54} jeweils unabhängig voneinander Wasserstoff oder C_1-C_8-Alkyl ist, das substituiert sein kann mit C_1-C_4-Alkoxy oder C_1-C_4-Alkoxy-C_1-C_4-Alkoxy.

5. Farbstoffe gemäß Anspruch 1, die Farbstoffe zum Färben einer Fasermischung sind, unfassend (1) Polyamid oder Polyurethanfasern und (2) Polyester oder Triacetatfasern.

Revendications

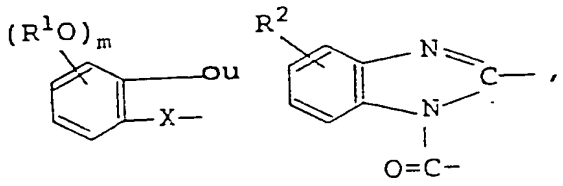
1. Colorants de type imide d'acide naphtalique, insolubles dans l'eau, représentés par la formule suivante :



(I)

dans laquelle :

- D représente



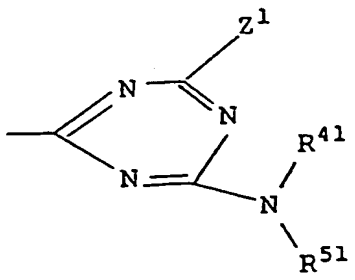
où R^1 représente alkyle en C_1-C_8, lequel peut être substitué, R^2 représente hydrogène, halogène, alkyle inférieur, alcoxy inférieur ou cyano, X représente oxygène ou soufre, et m vaut 0 ou 1 ;

- A représente phénylène, alkylène, aralkylène ou $-C_2H_4OC_2H_4-$;
- B représente oxygène, soufre ou

où R^3 représente hydrogène ou alkyle inférieur ;

- Y représente un cycle triazine, pyrimidine ou pyridazine, ayant au moins un atome d'halogène actif ; et
- n vaut 0 ou 1.

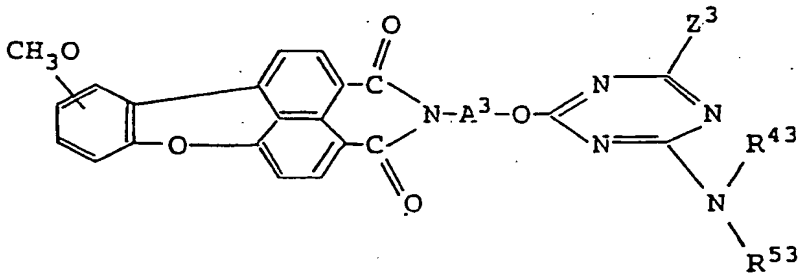
2. Colorants selon la revendication 1, dans lesquels Y représente un substituant de la formule suivante :



dans laquelle :

- Z^1 représente fluor ou chlore ;
- R^{41} et R^{51}, qui sont indépendants l'un de l'autre, représentent chacun hydrogène, alkyle en C_1-C_8 qui peut être substitué par alcoxy en C_1-C_4 ou alcoxy en C_1-C_4 -alcoxy en C_1-C_4, alcényle, aryle ou aralkyle, ou $-NR^{41}R^{51}$ représente un groupe hétérocyclique contenant de l'azote, à 6 chaînons, formé par la liaison de R^{41} et R^{51}.

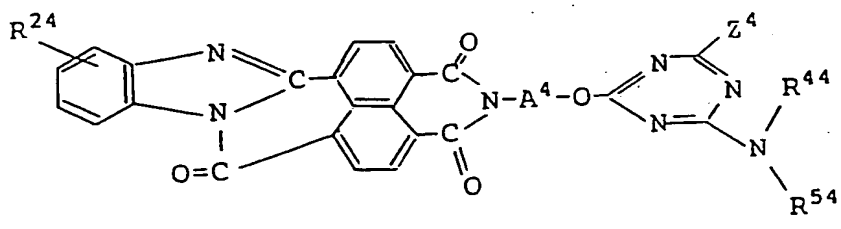
3. Colorants selon la revendication 1, qui sont représentés par la formule suivante :



dans laquelle :

- A^3 représente alkylène en C_1-C_3 ou aralkylène ;
- Z^3 représente fluor ou chlore ; et
- R^{43} et R^{53}, qui sont indépendants l'un de l'autre, représentent chacun hydrogène, ou alkyle en C_1-C_8 qui peut être substitué par alcoxy en C_1-C_4 ou alcoxy en C_1-C_4 - alcoxy en C_1-C_4.

4. Colorants selon la revendication 1, qui sont représentés par la formule suivante :



dans laquelle :

- A^4 représente alkylène en C_1-C_3 ou aralkylène ;
- R^{24} représente chlore, méthyle et méthoxy ;
- Z représente fluor ou chlore ; et
- R^{44} et R^{54}, qui sont indépendants l'un de l'autre, représentent chacun hydrogène, ou alkyle en C_1-C_8 qui peut être substitué par alcoxy en C_1-C_4 ou alcoxy en C_1-C_4 - alcoxy en C_1-C_4.

5. Colorants selon la revendication 1, qui sont des colorants pour teindre un mélange de fibres comprenant (1) des fibres de polyamide ou de polyuréthanne et (2) des fibres de polyester ou de triacétate.